Crystal structure of di(bis(cyclopentadienyl)titanocene) carbonate, $C_{42}H_{40}O_6Ti_4$

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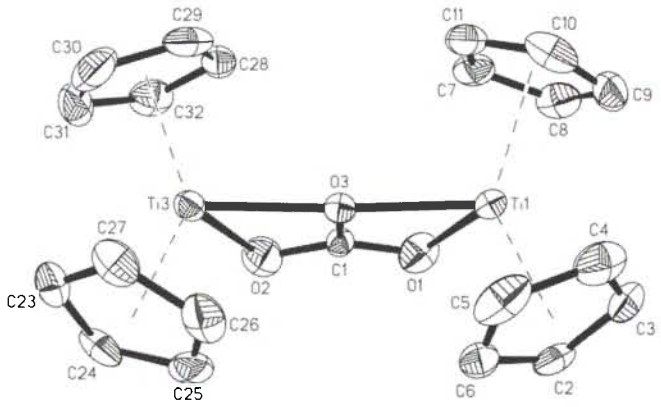

Abstract

$C_{42}H_{40}O_6Ti_4$, monoclinic, $P12_1/n1$ (No. 14), a = 19.522(4) Å, b = 7.891(2) Å, c = 25.100(5) Å, β = 96.52(3)°, V = 3841.6 Å^3, Z = 4, $R_{obs}(F)$ = 0.035, $wR_{all}(F^2)$ = 0.073, T = 293 K.

Source of material

To a solution of 480 mg (0.58 mmol) $(Cp_2Ti)_2$-μ-(η^4-2:3,6:7-PhHC=N-N-CHPh-CHPh-N-N=CHPh) in 20 ml of toluene was added 20 μl of H_2O and the solution was then saturated with carbon dioxide. As the brown reaction mixture was stirred for 24 hours at room temperature the color changed to dark blue. The solvent was evaporated in vacuo and the residue was crystallized at 278 K from THF/n-hexane (1:3) to yield 140 mg (58%) of the title compound.

Discussion

On studying the interaction of various titanocene complexes with carbon dioxide, there could be obtained mono-, bi- and tetranuclear species with different substituted Cp-ligands [1-3]. Herein we report on the structure of a postulated binuclear blue carbonate complex of titanocene $(Cp_2Ti)_2$ (μ_2,μ_2-CO_3). There are two symmetry independent molecules in the assymmetric unit.

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Table 1. Data collection and handling.

Crystal:	blue prism, size 0.2 × 0.3 × 0.5 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	8.48 cm^{-1}
Diffractometer, scan mode:	Stoe IPDS, 100 exposures, Δφ = 2°
$2\theta_{max}$:	48.6°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	10981, 5960
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 3473
$N(param)_{refined}$:	469
Programs:	SHELXS-86 [4], SHELXL-93 [5]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(2)	4e	0.5481(2)	0.1172(5)	0.4034(2)	0.063
H(3)	4e	0.5052(2)	0.1450(5)	0.3079(2)	0.071
H(4)	4e	0.5804(2)	−0.0225(6)	0.2554(2)	0.086
H(5)	4e	0.6738(2)	−0.1471(5)	0.3186(2)	0.087
H(6)	4e	0.6527(2)	−0.0630(5)	0.4105(2)	0.075
H(7)	4e	0.7272(2)	0.5379(5)	0.3252(2)	0.070
H(8)	4e	0.5989(2)	0.5554(5)	0.3088(2)	0.074
H(9)	4e	0.5608(2)	0.3364(6)	0.2399(2)	0.083
H(10)	4e	0.6655(3)	0.1888(6)	0.2157(2)	0.086
H(11)	4e	0.7662(2)	0.3143(6)	0.2680(2)	0.078
H(13)	4e	0.9301(2)	0.2656(6)	0.7218(2)	0.088
H(14)	4e	0.9893(2)	0.4277(6)	0.6561(2)	0.096
H(15)	4e	0.9263(3)	0.3768(7)	0.5675(2)	0.109
H(16)	4e	0.8275(3)	0.1935(7)	0.5779(2)	0.099
H(17)	4e	0.8280(2)	0.1283(5)	0.6737(2)	0.089
H(18)	4e	0.8923(2)	0.8285(6)	0.6692(2)	0.095
H(19)	4e	0.7640(2)	0.8028(6)	0.6636(2)	0.090
H(20)	4e	0.7383(3)	0.5778(8)	0.7255(2)	0.099
H(21)	4e	0.8475(4)	0.4627(7)	0.7693(2)	0.115
H(22)	4e	0.9423(3)	0.6206(7)	0.7359(2)	0.109
H(23)	4e	0.9718(2)	−0.1031(5)	0.4600(1)	0.065
H(24)	4e	0.8881(2)	−0.0248(5)	0.5229(1)	0.071
H(25)	4e	0.7699(2)	−0.0795(5)	0.4769(2)	0.078
H(26)	4e	0.7819(2)	−0.1937(5)	0.3867(2)	0.078
H(27)	4e	0.9057(2)	−0.2040(5)	0.3752(2)	0.071
H(28)	4e	0.8479(2)	0.4392(5)	0.3528(2)	0.066
H(29)	4e	0.8898(2)	0.1909(6)	0.3060(2)	0.077
H(30)	4e	0.9862(2)	0.0650(6)	0.3647(2)	0.101
H(31)	4e	1.0036(2)	0.2352(7)	0.4480(2)	0.100
H(32)	4e	0.9189(2)	0.4693(6)	0.4398(2)	0.079
H(33)	4e	0.5119(2)	0.1446(5)	0.5515(2)	0.080
H(34)	4e	0.5780(2)	0.0694(5)	0.6379(2)	0.066
H(35)	4e	0.7021(2)	0.0722(5)	0.6252(2)	0.074
H(36)	4e	0.7115(3)	0.1552(5)	0.5304(2)	0.091
H(37)	4e	0.5930(3)	0.2006(6)	0.4866(2)	0.100
H(38)	4e	0.6426(2)	0.7015(7)	0.6481(2)	0.097
H(39)	4e	0.6023(3)	0.4558(8)	0.6988(2)	0.101
H(40)	4e	0.5034(3)	0.3299(8)	0.6434(3)	0.123
H(41)	4e	0.4813(3)	0.4909(9)	0.5603(3)	0.126
H(42)	4e	0.5669(3)	0.7228(7)	0.5627(3)	0.116

Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	4*e*	0.7408(2)	0.2708(4)	0.4170(1)	0.031(2)	0.033(2)	0.037(2)	–0.002(2)	0.003(2)	0.001(2)
C(2)	4*e*	0.5676(2)	0.0682(5)	0.3750(2)	0.050(2)	0.058(3)	0.054(2)	–0.023(2)	0.022(2)	–0.005(2)
C(3)	4*e*	0.5436(2)	0.0830(5)	0.3218(2)	0.039(2)	0.065(3)	0.073(3)	–0.017(2)	0.002(2)	0.004(2)
C(4)	4*e*	0.5858(2)	–0.0096(6)	0.2925(2)	0.086(3)	0.078(4)	0.054(3)	–0.044(3)	0.014(3)	–0.023(2)
C(5)	4*e*	0.6377(2)	–0.0801(5)	0.3277(2)	0.065(3)	0.031(3)	0.127(4)	–0.008(2)	0.039(3)	–0.019(3)
C(6)	4*e*	0.6260(2)	–0.0325(5)	0.3789(2)	0.054(3)	0.050(3)	0.081(3)	–0.021(2)	–0.006(2)	0.024(2)
C(7)	4*e*	0.6989(2)	0.4710(5)	0.3014(2)	0.066(3)	0.048(3)	0.064(3)	–0.015(2)	0.012(2)	0.014(2)
C(8)	4*e*	0.6271(2)	0.4814(5)	0.2924(2)	0.069(3)	0.035(3)	0.085(3)	0.020(2)	0.028(2)	0.020(2)
C(9)	4*e*	0.6060(2)	0.3590(6)	0.2540(2)	0.058(3)	0.074(3)	0.070(3)	–0.014(2)	–0.016(2)	0.034(3)
C(10)	4*e*	0.6647(3)	0.2764(6)	0.2404(2)	0.111(4)	0.064(3)	0.040(2)	0.011(3)	0.012(3)	0.007(2)
C(11)	4*e*	0.7206(2)	0.3462(6)	0.2695(2)	0.056(3)	0.083(4)	0.059(3)	0.011(2)	0.021(2)	0.030(2)
C(12)	4*e*	0.7415(2)	0.5284(4)	0.5729(1)	0.036(2)	0.032(2)	0.046(2)	–0.002(2)	0.007(2)	0.002(2)
C(13)	4*e*	0.9166(2)	0.2719(6)	0.6852(2)	0.070(3)	0.075(4)	0.070(3)	0.033(3)	–0.013(3)	0.005(3)
C(14)	4*e*	0.9500(2)	0.3612(6)	0.6487(2)	0.039(2)	0.065(4)	0.136(5)	0.009(2)	0.014(3)	–0.005(3)
C(15)	4*e*	0.9148(3)	0.3333(7)	0.5997(2)	0.089(4)	0.106(5)	0.085(4)	0.047(3)	0.044(3)	0.019(3)
C(16)	4*e*	0.8598(3)	0.2313(7)	0.6055(2)	0.070(4)	0.077(4)	0.097(4)	0.036(3)	–0.012(3)	–0.043(3)
C(17)	4*e*	0.8601(2)	0.1942(5)	0.6585(2)	0.058(3)	0.034(3)	0.131(5)	0.010(2)	0.013(3)	0.009(3)
C(18)	4*e*	0.8679(2)	0.7536(6)	0.6885(2)	0.067(3)	0.041(3)	0.129(4)	–0.012(2)	0.010(3)	–0.022(3)
C(19)	4*e*	0.7961(2)	0.7389(6)	0.6853(2)	0.079(4)	0.050(3)	0.093(4)	0.014(2)	0.001(3)	–0.018(3)
C(20)	4*e*	0.7821(3)	0.6141(8)	0.7196(2)	0.072(3)	0.097(5)	0.079(3)	–0.007(3)	0.015(3)	–0.048(3)
C(21)	4*e*	0.8429(4)	0.5500(7)	0.7442(2)	0.150(6)	0.079(4)	0.055(3)	–0.004(4)	–0.003(3)	–0.021(3)
C(22)	4*e*	0.8956(3)	0.6373(7)	0.7254(2)	0.084(4)	0.067(4)	0.111(4)	0.017(3)	–0.035(3)	–0.039(3)
C(23)	4*e*	0.9241(2)	–0.1106(5)	0.4532(1)	0.053(2)	0.047(3)	0.059(2)	0.013(2)	–0.005(2)	0.005(2)
C(24)	4*e*	0.8774(2)	–0.0671(5)	0.4884(1)	0.086(3)	0.052(3)	0.038(2)	0.018(2)	0.003(2)	0.015(2)
C(25)	4*e*	0.8111(2)	–0.0981(5)	0.4625(2)	0.063(3)	0.042(3)	0.094(3)	0.007(2)	0.028(3)	0.032(2)
C(26)	4*e*	0.8179(2)	–0.1612(5)	0.4121(2)	0.073(3)	0.029(3)	0.087(3)	–0.005(2)	–0.017(3)	0.006(2)
C(27)	4*e*	0.8870(2)	–0.1678(5)	0.4057(2)	0.082(3)	0.038(3)	0.056(3)	0.010(2)	0.002(2)	–0.002(2)
C(28)	4*e*	0.8842(2)	0.3687(5)	0.3659(2)	0.046(2)	0.052(3)	0.066(3)	–0.011(2)	0.002(2)	0.026(2)
C(29)	4*e*	0.9074(2)	0.2299(6)	0.3398(2)	0.078(3)	0.073(4)	0.045(2)	–0.019(3)	0.024(2)	0.007(2)
C(30)	4*e*	0.9609(2)	0.1600(6)	0.3724(2)	0.053(3)	0.072(4)	0.136(5)	0.011(2)	0.045(3)	0.028(3)
C(31)	4*e*	0.9707(2)	0.2553(7)	0.4188(2)	0.047(3)	0.091(4)	0.106(4)	–0.025(3)	–0.024(3)	0.048(3)
C(32)	4*e*	0.9234(2)	0.3853(6)	0.4144(2)	0.074(3)	0.056(3)	0.068(3)	–0.025(3)	0.009(2)	0.001(2)
C(33)	4*e*	0.5597(2)	0.1377(5)	0.5582(2)	0.057(3)	0.065(3)	0.077(3)	–0.022(2)	–0.001(2)	0.002(2)
C(34)	4*e*	0.5964(2)	0.0951(5)	0.6063(2)	0.063(3)	0.049(3)	0.055(2)	–0.016(2)	0.020(2)	0.005(2)
C(35)	4*e*	0.6656(2)	0.0972(5)	0.5992(2)	0.052(3)	0.032(3)	0.098(3)	–0.003(2)	–0.003(2)	0.005(2)
C(36)	4*e*	0.6710(3)	0.1434(5)	0.5463(2)	0.083(3)	0.046(3)	0.111(4)	–0.021(2)	0.068(3)	–0.024(3)
C(37)	4*e*	0.6048(3)	0.1682(6)	0.5221(2)	0.132(5)	0.072(4)	0.045(2)	–0.047(3)	0.010(3)	–0.007(2)
C(38)	4*e*	0.6058(2)	0.6305(7)	0.6368(2)	0.054(3)	0.063(4)	0.126(4)	0.017(3)	0.014(3)	–0.036(3)
C(39)	4*e*	0.5834(3)	0.4931(8)	0.6652(2)	0.099(4)	0.086(4)	0.074(3)	0.031(3)	0.042(3)	–0.008(3)
C(40)	4*e*	0.5284(3)	0.4237(8)	0.6342(3)	0.061(4)	0.088(5)	0.169(6)	0.007(3)	0.062(4)	–0.021(5)
C(41)	4*e*	0.5160(3)	0.5129(9)	0.5880(3)	0.057(3)	0.097(5)	0.157(6)	0.035(4)	–0.010(4)	–0.034(4)
C(42)	4*e*	0.5638(3)	0.6421(7)	0.5894(3)	0.091(4)	0.059(4)	0.144(5)	0.040(3)	0.034(4)	0.015(3)
O(1)	4*e*	0.6777(1)	0.3353(3)	0.4089(1)	0.060(2)	0.073(2)	0.073(2)	–0.004(1)	0.014(1)	–0.006(2)
O(2)	4*e*	0.7918(1)	0.2812(3)	0.4565(1)	0.073(2)	0.067(2)	0.063(2)	–0.000(2)	0.006(2)	0.000(1)
O(3)	4*e*	0.7559(1)	0.1731(3)	0.37660(7)	0.037(1)	0.032(2)	0.030(1)	0.0013(9)	0.0071(9)	–0.0039(9)
O(4)	4*e*	0.6861(2)	0.5278(4)	0.5366(1)	0.081(2)	0.070(2)	0.074(2)	–0.011(2)	0.005(2)	0.004(2)
O(5)	4*e*	0.7330(1)	0.4368(3)	0.61613(8)	0.039(1)	0.035(2)	0.038(1)	–0.003(1)	0.009(1)	0.009(1)
O(6)	4*e*	0.8032(1)	0.5964(4)	0.5745(1)	0.069(2)	0.081(2)	0.093(2)	–0.004(2)	0.011(2)	0.023(2)
Ti(1)	4*e*	0.65469(3)	0.21577(7)	0.33289(2)	0.0329(3)	0.0305(4)	0.0370(3)	–0.0018(3)	0.0084(3)	–0.0018(3)
Ti(2)	4*e*	0.83821(3)	0.48597(8)	0.65077(2)	0.0401(4)	0.0314(4)	0.0480(4)	0.0011(3)	0.0052(3)	0.0022(3)
Ti(3)	4*e*	0.85901(3)	0.12645(8)	0.41541(2)	0.0388(4)	0.0332(4)	0.0357(3)	0.0007(3)	0.0028(3)	0.0044(3)
Ti(4)	4*e*	0.62640(3)	0.38128(8)	0.58799(2)	0.0377(4)	0.0394(4)	0.0464(4)	0.0012(3)	0.0093(3)	0.0004(3)

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